

# Kinetics of Particles Adsorption Processes Driven by Diffusion.

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The kinetics of the deposition of colloidal particles onto a solid surface is analytically studied. We take into account both the diffusion of particles from the bulk as well as the geometrical aspects of the layer of adsorbed particles. We derive the first kinetic equation for the coverage of the surface (a generalized Langmuir equation) whose predictions are in agreement with recent simulation results where diffusion of particles from the bulk is explicitly considered.

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The adsorption of colloidal particles onto adsorbing surfaces is a very common phenomenon in many fields of Biology and Chemical-Physics. The deposition of bacteria on teeth is an example of such a process. There are many other systems in which suspensions are in contact with adsorbing solid surfaces. The adsorption of latex spheres onto a flat solid surface is a simple experimental model system, on which considerable work has been done. An optical microscope permits the direct observation of structural properties of the adsorbed layer [11,12].

This apparently simple phenomenon involves several fundamental processes that govern the kinetic behavior of the system and the structure of the adsorbed layer. First, the attractive potential that characterizes the adsorbing surface plays an essential role. Depending on the strength of this potential, adsorbed particles can either desorb or move laterally or remain irreversibly adsorbed. Second, the kinetics of the adsorption is strongly influenced by particle transport from the bulk to the surface. It depends, for instance, on whether gravity or diffusion dominates the dynamics of the particles in the bulk. Third, the adsorbing particles interact with the adsorbed ones in the vicinity of the surface. This interaction is repulsive for stable colloidal dispersions and, therefore, it is responsible for the saturation of the adsorbing surface, the so-called *blocking effect*.

Theories have been proposed to analyze the contribution of these effects to the kinetics of the adsorption of colloidal particles. A very common model is the *random sequential adsorption* (RSA) [1], introduced to generate the structure of a layer of irreversibly adsorbed colloidal particles. In this model, the adsorbing particles are deposited sequentially at random. The overlaps are forbidden so that, when in a trial an adsorbing particle overlaps an adsorbed one, this trial is rejected and one proceeds with a new one. Clearly, RSA takes the excluded volume effect into account but it cannot deal with the transport process of the particles from the bulk to the surface. However, a kinetic equation for the RSA model

has been proposed [2]. If one defines the coverage of a two-dimensional surface  $\theta$  as  $\pi R^2 \rho_s$ ,  $\rho_s$  being the number of adsorbed particles per unit area, and  $R$  the radius of the particles, one then writes

$$\frac{\partial \theta}{\partial t} = K_a \rho_B \Phi_{RSA}(\theta). \quad (1)$$

Here  $K_a$  is a kinetic coefficient,  $\rho_B$  is the concentration in the bulk and  $\Phi_{RSA}(\theta)$  is the available area at a given coverage for a new particle to adsorb.  $\Phi_{RSA}$  was first obtained by Widom [3].

Some effort has also been made in constructing a model incorporating a description of the transport of adsorbing particles from the bulk. For spherical particles, heuristic arguments allowed Shaaf *et al.* [4] to describe the kinetics of irreversible adsorption for a system near surface saturation. When diffusion is explicitly considered, these authors found that the time-dependence of the surface coverage is changed with respect to that obtained from the pure RSA model (eq. (1)). Tarjus and Viot [6] later proposed an analytic (1+1)-dimensional model, in which hard disks were adsorbed onto a line, in order to give more insight on the previous results of Shaaf *et al.* From ref. [6], one can infer that the shape of the particles plays a significant role in the time-dependence of the coverage near saturation. Currently, for three dimensional systems the kinetics of adsorption over all time ranges is only known from simulations [5].

In this letter, we propose a model taking into account both the diffusion of the particles from the bulk and the saturation of the surface due to the blocking effect. Our aim is primarily to derive a kinetic equation (*generalized Langmuir equation*) describing the time-evolution of the coverage for a three-dimensional system. Our equation is valid not only near saturation but also at intermediate times, when the surface is only partially covered. The results issued from our work are in good agreement with recent simulations [5] (Fig.1). Our secondary aim is to show that eq. (1) corresponds to the adsorption of dif-

fusing cylinders. This confirms previous authors' claims as to the crucial role played by the shape of the particles in the kinetics of adsorption.

The following analysis can be applied to a large class of systems, provided that they meet the following requirements; (i) the attractive potential, responsible for the adsorption of the particles on the surface, is large enough so that the adsorption can be regarded as irreversible. Then the particles are not observed to desorb or to diffuse laterally on the surface; (ii) the surface-particle as well as the particle-particle potential is of short range, much smaller than the size of the particles; (iii) diffusion dominates over gravitational effects in the dynamics of the adsorbing particles, thus the Péclet number ( $Pé = mgR/kT$ , where  $m$  is the mass of the particles,  $g$  is the acceleration of the gravity and  $kT$  is the thermal energy) of the system is much smaller than the unity.

The procedure adopted here is to consider that the system of adsorbing particles is in local equilibrium, so that a *local* chemical potential can be defined [7–9]. Here, the local equilibrium hypothesis is assumed since Brownian motion permits the particles to explore large regions in space before they get adsorbed. Thus, one expects that the overall adsorption process is not determined by the local inhomogeneities of the layer of adsorbed particles but by its global properties, in the spirit of a mean field approach. Finally, for the system under scrutiny, the only relevant direction will be that orthogonal to the plane (the  $z$ -direction) since adsorption will be responsible for an overall density gradient depending only on  $z$ .

Therefore, considering that the suspension of the adsorbing particles is dilute, one can write the local chemical potential as

$$\mu(\gamma) = kT \ln[\rho(\gamma)] - kT \ln \Phi(\theta, \gamma) \quad (2)$$

where  $\gamma \equiv z/2R$  is the dimensionless coordinate in the

$z$ -direction,  $R$  being the radius of the particles. The origin of coordinates is thus taken at a distance  $R$  from the adsorbing plane so that  $z = 0$  coincides with the centers of the adsorbed particles. Therefore, it is in the region  $0 \leq \gamma \leq 1$  that the interaction between the adsorbing and the adsorbed particles takes place. This region will be referred to as the *interaction layer* from now on. In eq. (2), the first term in the right hand side comes from the configurational contribution as in an ideal gas. The second term accounts for the accessible area at a given height  $\gamma$  and at a given coverage  $\theta$ , through the available surface function  $\Phi(\theta, \gamma)$ , which comes from an average over the configurations of the deposited particles at a fixed coverage [13]. Note that, for a given coverage, the change of the available surface function with  $\gamma$  is only due to the shape of the particles. It is easy to see that the area excluded at  $\gamma$  by a single adsorbed sphere is simply  $4\pi R^2(1 - \gamma^2)$ . Thus, the available surface function can approximately be written as a function of one argument, according to  $\Phi(\theta, \gamma) \simeq \Phi(\theta(1 - \gamma^2))$ . In this approximation an additional explicit dependence in  $\gamma$  is ignored, due to the fact that in performing the average over the configurations the true radius of the particles is not the scaled one at a given  $\gamma$ . This explicit dependence is not too important for our purposes since the kinetics mainly depends on the behavior of  $\Phi(\theta, \gamma)$  for  $\gamma$  near 0, which corresponds to the bottle-neck for the whole process. We will further assume that the chemical potential of the bulk corresponds to that of a dilute suspension of particles,  $\mu_B = kT \ln[\rho_B]$ .

Recent experimental results [10] indicate that the geometrical aspects of the adsorbed layer for real systems at small Péclet number are practically indistinguishable from those obtained from RSA filling rules. Therefore, this allows us to further assume that  $\Phi(\theta, \gamma) \simeq \Phi_{RSA}(\theta(1 - \gamma^2))$ . Using the uniform approximation for the  $\theta$ -dependence of  $\Phi_{RSA}$  as given in ref. [14], we can finally write

$$\Phi(\theta, \gamma) = \frac{(1 - x(1 - \gamma^2))^3}{1 - 0.812x(1 - \gamma^2) + 0.234x^2(1 - \gamma^2)^2 + 0.084x^3(1 - \gamma^2)^3} \quad (3)$$

where  $x \equiv \theta/\theta_\infty$ ,  $\theta_\infty$  being the coverage at saturation.

To proceed further, we will analyze the flux of particles going to the surface. Adsorbing particles satisfy a continuity equation of the form

$$\frac{\partial}{\partial t} \rho(\gamma, t) = - \frac{\partial}{\partial \gamma} J(\gamma, t) \quad (4)$$

where we have considered that the variables depend only on the  $z$ -direction through  $\gamma$ , and on the time. Since the gradient of the chemical potential (2) is the thermody-

namic force responsible for the flux of particles, one can write

$$J(\gamma) = -L(\gamma) \frac{\partial \mu(\gamma)}{\partial \gamma} \quad (5)$$

where we have assumed a linear relation between the flux  $J(\gamma)$  and the thermodynamic force  $\partial \mu(\gamma)/\partial \gamma$ ,  $L(\gamma)$  being a phenomenological coefficient in the spirit of Onsager's approach [15]. In this way, from eqs. (4) and (5) we arrive to a Smoluchowski equation for the density of the adsorbing particles inside the interaction layer

$$\frac{\partial}{\partial t}\rho = \frac{\partial}{\partial \gamma} \frac{D}{R^2} \left[ \frac{\partial}{\partial \gamma} \rho - \rho \frac{\partial}{\partial \gamma} \ln \Phi \right] \quad (6)$$

where we have defined the *diffusion coefficient*  $D \equiv kT L R^2 / \rho$  assumed as constant from now on. The adsorbed particles induce an entropic barrier, which depends on their shape and on the coverage, through which the adsorbing ones have to diffuse to reach the wall. Crucial is to note that eq. (6) differs from the Smoluchowski equation obtained by Shaaf *et al* [4]. The cross-sectional area in ref [4] is defined only near saturation and the master equation used have no meaning out of this limit. Thus the presence of  $\Phi$  in the Smoluchowski equation (6) is not trivial.

We will now derive the kinetic equation. We assume that the process is quasistationary  $\partial \rho / \partial t \simeq 0$ . This means that  $J(\gamma)$  is a constant, standing for the fact that no accumulation of adsorbing particles in the interaction layer occurs. Thus, mass conservation leads to  $J(\gamma) = J_s$ , where  $J_s$  is the flux of particles reaching the adsorbing surface. We consider here that the density of particles in the bulk is the control parameter and thus express  $J_s$  in terms of  $\rho_B$ , with the boundary conditions

$$\mu(\gamma = 1) = \mu_B, \quad (7)$$

$$\mu(\gamma = 0) \rightarrow -\infty \quad (8)$$

The first boundary condition assumes that the chemical potential is continuous through the upper boundary of the interaction layer. The second stands for an irreversible adsorption process. It is equivalent to imposing  $\rho(\gamma = 0) = 0$ , according to eq.(2), meaning that there are no free particles in contact with the surface. In this way, we can obtain the flux of particles reaching the surface in terms of  $\rho_B$  by solving the differential equation

$$J_s = -\frac{D}{R^2} \left[ \frac{\partial}{\partial \gamma} \rho - \rho \frac{\partial}{\partial \gamma} \ln \Phi \right] \quad (9)$$

with boundary conditions specified in eqs. (7) and (8). We then arrive at

$$J_s = -\frac{D}{R^2} \rho_B I(\theta) \quad (10)$$

where

$$I(\theta) = \frac{1}{\int_0^1 \frac{1}{\Phi(\theta, \gamma)} d\gamma} \quad (11)$$

Therefore, the equation for the density of the adsorbed particles has the form

$$\frac{\partial \rho_s}{\partial t} = -J_s = \frac{D}{R^2} \rho_B I(\theta) \quad (12)$$

This equation can be rewritten in terms of the coverage by multiplying both sides by  $\pi R^2$ , yielding a generalized Langmuir equation

$$\frac{\partial \theta}{\partial t} = K_a \rho_B I(\theta) \quad (13)$$

where we have defined the kinetic coefficient  $K_a = D\pi$ . Therefore, the main result of this letter is a equation describing the covering of an adsorbing surface when diffusion as well as the blocking effect are important.

The asymptotic time-dependence near saturation is obtained by analyzing the behavior of  $I(\theta)$  when  $\theta \rightarrow \theta_\infty$ . In this limit, this function behaves as  $I(\theta) \sim (\theta - \theta_\infty)^{5/2}$ . Inserting this asymptotic behavior in eq. (13) we find that  $\theta - \theta_\infty \sim t^{-2/3}$ . Therefore, our equation recovers the power law behavior near saturation [4]. However, we can go beyond the calculations of ref. [4] because eq. (13) gives the evolution of the coverage in all the time range. We have to precise at this point that at the very beginning of the deposition process, the quasistationary conditions break down. Thus, our analysis is valid only after this initial time range which is of the order of  $R^2/D$ . In particular, for all values of  $\theta/\theta_\infty$  we find a remarkable agreement between  $I(\theta)$  obtained here and the results reported in ref. [5], from simulations of diffusing spheres (Fig. 1). The underlying physics leading the kinetics of the system is independent of the distance  $h$  at which one place the particle reservoir keeping constant  $\rho_B$ . However, the quasistationary condition critically depend on this distance due to the fact that the density profile relaxes with a time scale  $h^2/D$ . Note, however, that in ref. [5] the reservoir is located at a distance of the order of  $R$ , being then justified the comparison of these simulations with our calculations.

Let us now consider a system in which the particles are cylinders (radius  $R$  and heigth  $2R$ ) that diffuse with their axis perpendicular to the adsorbing surface. In this case, the available surface function  $\Phi$  is independent of  $\gamma$ . Thus, from eq. (11), one straightforwardly gets  $I(\theta) = \Phi_{RSA}(\theta)$ . Therefore, for this system we have found the same kinetic equation as that proposed for the RSA model (eq. (5)). Obviously, the asymptotic behavior for the coverage near saturation for diffusing cylinders gives the RSA power law decay  $\theta - \theta_\infty \sim t^{-1/2}$ . Particles of different shape can also be studied. In particular, one can consider revolution bodies wich offer an available surface function of the form  $\Phi(\theta(1 - \gamma^{2n})^{1/n})$ , which would correspond to spheres for  $n = 1$ , and to cylinders for  $n \rightarrow \infty$ . For intermediate values of  $n$ , these particles look like cylinders with round edges. One can then determine the kinetic equations for such objets and find the corresponding power law behavior near saturation. The

asymptotic behavior depends on  $n$  and has the form  $\theta - \theta_\infty \sim t^{2n/(1-4n)}$ .

Our analysis, therefore, gives an interpretation of the previous simulation results [5], pointing out the collective effect of diffusion, blocking effect and the shape of the particles, on the kinetics of adsorption. Due to the generality of the basic statements underlying our theory, one can envisage its use to the study of the kinetics of more complex systems as, for instance, suspensions of elongated particles, provided that the structural properties of the adsorbed layer are given.

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